CANADIAN JOURNAL OF RESEARCH

VOLUME 21 OCTOBER, 1943 NUMBER 10

CONTENTS

SECTION A.—PHYSICAL SCIENCES

Page

Absorption of Light by Small Drops of Water—*R. Ruedy* - - 79

SECTION B.—CHEMICAL SCIENCES

Froth Flotation of Rubber and Resin Components of Milkweed and Other Plants that Contain Resins, Rubber, Balata, or Related Gummy Substances—*Wm. T. Turral, J. Klassen, and H. Smedley* - - - - - - - - - - - - 195

The Physical States of Anhydrous Sodium Soaps—*W. Gallay and I. E. Puddington* - - - - - - - - - 202

The Effect of Certain Addition Agents on the Physical States of Sodium Soaps—*W. Gallay and I. E. Puddington* - - - 211

The Rubber Hydrocarbon of *Asclepias syriaca* L.—*E. B. Paul, A. L. Blakers, and R. W. Watson* - - - - - - - 219

NATIONAL RESEARCH COUNCIL
OTTAWA, CANADA

Publications and Subscriptions

The Canadian Journal of Research is issued monthly in four sections, as follows:

A. Physical Sciences
B. Chemical Sciences
C. Botanical Sciences
D. Zoological Sciences

For the present, Sections A and B are issued under a single cover, as also are Sections C and D, with separate pagination of the four sections, to permit separate binding, if desired.

Subscription rates, postage paid to any part of the world are as follows:

	Annual	*Single Copy*
A and B	$ 2.50	$ 0.50
C and D	2.50	0.50
Four sections, complete	4.00	—

The Canadian Journal of Research is published by the National Research Council of Canada under authority of the Chairman of the Committee of the Privy Council on Scientific and Industrial Research. All correspondence should be addressed:

National Research Council, Ottawa, Canada.

Notice to Contributors

Fifty reprints of each paper are supplied free. Additional reprints, if required, will be supplied according to a prescribed schedule of charges.

Canadian Journal of Research

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOL. 21, SEC. A. OCTOBER, 1943 NUMBER 10

ABSORPTION OF LIGHT BY SMALL DROPS OF WATER[1]

BY R. RUEDY[2]

Abstract

When the extinction coefficient k in the attenuation formula $I/I_0 = (\exp) - kz$ for a beam of radiations of initial intensity I_0, and intensity I after travelling a distance z in water, changes from about 10^{-4}, the value measured in the visible region, to 10^3, the value reached in some infrared absorption bands for water in bulk, the coefficient of extinction for water in very small drops, calculated according to Mie's theory, increases as long as the wave-length used is larger than the radius a of the particle. With larger drops, that is, when the wave-lengths are shorter than the radius, the coefficient for the extinction by water particles with strong absorption is smaller than that for perfectly transparent particles. However, the change does not exceed about 10% even where the absorption is strongest, and it is negligible when wave-lengths smaller than one micron are considered. The main features of the coefficient of extinction per unit area of the drop remain unchanged by absorption; first there is a rapid increase with decreasing wave-lengths for particles of a given diameter until the ratio $a/\lambda = 1/n$ (the reciprocal of the index of refraction) is reached, then follows a more gradual approach to a maximum, slightly less than $4\pi a^2$ as $2a/\lambda$ increases to unity, and finally, when λ is quite small, a decrease towards a constant value after a small number of fluctuations that reach their greatest amplitudes near the integer multiples of $2a/\lambda$.

Introduction

Mie's solution of the equations governing the propagation of light in a medium containing spherical obstacles was used by Blumer in order to find out to what extent the light scattered by extremely small drops of water accounts for the colours of the sky before sunrise and after sunset. The droplets considered had diameters equal to one-half wave-length or one wave-length at the most (3). Later the calculations were extended to larger water drops for which the diameters were several times, up to 10 times, the wave-length of light (8). The results of the theory were tested by experiments with artificial fogs or clouds.

Pokrowski (9) worked with water drops formed by sudden condensation of water vapour. The average diameter of the drops in his experiments was considerably smaller than the wave-lengths in the visible spectrum, the greatest ratio between diameter and wave-length being about one-fifth. The artificial clouds investigated by Paranjpe, Naik, and Vaidya (8) are formed above a small quantity of water, kept inside a flask of 12 litres capacity, by connecting this container suddenly to a large tank in which a suitable low pressure has been created by means of a vacuum pump. When a sudden expansion of the desired magnitude is effected, a fixed quantity of vapour is

[1] *Manuscript received July 3, 1943.*

Contribution from the Research Plans and Publications Section, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1150.

[2] *Research Investigator.*

available for condensation, and this vapour is distributed around a number of solid nuclei in the flask. By controlling the number of dust nuclei sharing in the supply of vapour during the condensation, a cloud with drops of almost any desired size can be produced, provided condensation on the walls is reduced by wetting the inside surface at the beginning of the test. The dust particles, about 0.05 μ in diameter, are obtained by burning a stick of incense in a large cupboard. From the cupboard the dusty air diffuses into the flask. As larger and larger drops are used, the light, instead of being scattered in all directions, gathers more and more into single straight beams as wide as the obstacles, the familiar rays of light.

Mie's theory of the scattering of light by small spherical particles proved to be useful also in another problem—in the study of the absorption of light by water particles. As a result of a rather unexpected observation, namely, a maximum in the amount of light transmitted by the water droplets in an artificial fine mist when the wave-length is in the neighbourhood of 0.490 μ, Stratton and Houghton (13) calculated the absorption for the whole range of the ratios of diameter to wave-length, $2a/\lambda$, between 0 and 13, and found satisfactory agreement between these results and the values given by the particular mist.

The water droplets studied were produced by condensing low pressure steam, in a zinc-lined box 300 cm. in length and about 25 cm. square in cross-section, on the nuclei normally present in the air. As seen in the microscope, the droplets were uniform in size and ranged from about 2 to 3 μ in diameter, whereas natural fog particles are known to measure from 5 to 20 μ and more.

Practical Applications of the Theory

An accurate knowledge of the scattering and absorption of light by small drops is also of help in the study of the condensation of steam flowing through nozzles, to mention only one important application proposed by Stodola (12). When, after having been forced through the constriction of a nozzle, steam is allowed to expand in the divergent portion of the nozzle, it begins to condense almost as soon as it has reached the saturation point, actually after about 3 or 4% supersaturation has been attained. The condensed portion of the steam gives up its latent heat, thus causing the density of the remaining vapour to decrease and the pressure to rise unless the increase in the volume of the vapour is fully compensated for by an increase in the velocity of flow. When a beam from a carbon arc is directed along the axis of the nozzle, the condensation can be detected by means of the light scattered at right angles to the flow (15). As observed through a window, the entering steam, supersaturated by throttling, is quite transparent, but when condensation is allowed to occur, a dense sky-blue mist appears, indicating the presence of water droplets too small to be seen. Should the droplets evaporate again farther along the nozzle, because of recompression, a dark region reveals the absence of drops; this is followed once more by the blue of scattered light

where the pressure falls below the saturation point (10). In the work described (15), steam at about 20 lb. per sq. in. gauge pressure and at 287° F. flows against a back pressure of 15 lb. abs. through a convergent–divergent nozzle. The nozzle is about $6\frac{7}{8}$ in. long and 2 in. wide at the entrance. The constricted portion has a constant radius of curvature of $\frac{3}{4}$ in. The length of this curved portion is equal to one-quarter of the circumference of the circle of radius $\frac{3}{4}$ in., so that the width is $\frac{1}{2}$ in. at the narrowest point, before the nozzle begins to diverge at a constant angle of 12°. The light is completely plane polarized when observed at right angles to the incident beam. From an equation given by Helmholtz for the vapour pressure of droplets in equilibrium with superheated steam, the radius of the droplets is computed to lie between 5×10^{-10} and 10×10^{-10} m., whereas the average wavelength of the arc light is about 0.6×10^{-6} m. Such drops would contain a few to five hundred molecules but the lower limit of the range over which the vapour pressure equation holds is not known (10).

When the length of the constricted portion of the nozzle is not negligible, but measures about one inch, so that the pressure gradient near the constriction is more uniform, the space close to the constriction is faintly blue, the colour denoting the beginning of condensation; at a certain cross-section the diffuse mist is cut off by the sharp boundary of a column of more intense blue corresponding to more copious liquefaction of the main mass of vapour. When the cloud formed during the initial condensation is viewed in a direction that forms an acute angle with the direction of the beam, the space occupied by the hazy cloud is seen to be traversed by transverse green, yellow, orange, and red bands, the red light being immediately lost in the more intense blue light emitted by the head of the main column of water droplets. When this blue colour disappears because of recompression of the steam, the red remains visible. The light other than blue is only partially polarized, and the intensity is much greater in the direction along which the light travels than at right angles to the beam. When, however, instead of looking back towards the converging portion, the eye views the constriction at a right angle, the whole cloud appears to be blue, the intensity increasing in the direction of the steam jet. The appearance of the various colours is taken as a sign of rapid growth of the particles from 10×10^{-10} m. in radius to about 0.6×10^{-6} m. radius. The long throat would retard the rapidity of expansion and give the drops time to grow. Further growth is apparently halted by the onset of the main condensation. The velocity of the steam jet, a few hundred metres per second, does not, at any rate, favour the formation of large drops.

In a convergent–divergent nozzle designed to produce a perfectly uniform pressure drop per unit length along the nozzle axis—by making its throat unusually long—different colours are scattered by the moisture particles even after the main condensation or ultimate condensation has occurred. The preliminary condensation is indicated by a blue haze at the half-way point of

the nozzle; a little farther on the strong blue colour denoting ultimate condensation appears; there follow yellow, orange, and red colours as the nozzle outlet is approached (10).

Growth also occurs in divergent nozzles when the angle of divergence is less than 2°, the colours changing from saffron to violet purple, green, and saffron again when the angle of observation is less than 90° to the incident light. If the angle of observation is greater than 90° so that the beams seen are a mixture of reflected and of diffracted light, the entire nozzle seems to be filled with a whitish-blue haze (16). Rapid growth of droplets occurs in many converging nozzles.

The presence of large droplets in a steam jet is undesirable because they are most destructive to the low-pressure blades of steel turbines. The drops apparently form during the pressure rise but their temperature does not increase rapidly. They are cooler than the steam. If the steam is superheated by only a few degrees the colours disappear.

Dry steam, also, scatters light, and a beam from an electric arc can be plainly seen in an atmosphere of superheated steam as a dark blue band against a perfectly black background. But whenever drops of water cross the beam, they stand out by virtue of the much stronger intensity of the scattered light (15).

With every nozzle that is tested, the initial condensation always scatters light of a blue colour. It is to be expected that the smallest drops scatter violet light more strongly than blue light. Attempts to detect the presence of violet scattering by employing special filters and photographic plates show that for some reason, as yet obscure, condensation is not occurring at any place other than where the eye can detect it (10). The absence of violet may indicate the lower limit in the size of the water droplets during condensation.

Absorption of Light by Water

In all the previous work mentioned, the water was considered to be an ideal dielectric without conduction and absorption at any frequency. It is only too well known that even in the visible region, water is not perfectly transparent. The transparency decreases when certain foreign materials are present; it increases with the number of distillations, and is a general measure of its purity, but even the purest water absorbs an appreciable amount of light in the red region of the spectrum. In the region to which the eye is most sensitive, between 0.5 and 0.6 μ, the absorption is least (Table I).

Aqueous solutions of uncoloured salts that do not form hydrates absorb light nearly to the same extent as water free from salts, but solutions of salts that form hydrates absorb the light slightly less than does the same thickness of pure water.

TABLE I

EXTINCTION COEFFICIENT k OF WATER IN BULK, ACCORDING TO THE ATTENUATION FORMULA $I/I_0 = \epsilon^{-kz}$

Wave-length, μ	Aschkinass 1895 (1)*	Lange and Schusterius (6)**	Clarke and James 1939	
			(4)***	(4)†
0.45	0.0002			0.0001
0.475	0.0002			0.0001
0.5	0.0002	0.0025		0.0001
0.525	0.00015		0.0004	
0.55	0.00036	0.0017	0.0007	
0.575	0.0002			
0.6	0.00163	0.0030	0.0018	
0.625	0.00223			
0.65	0.00255	0.0046	0.0026	0.0033
0.675	0.00329	0.0048		
0.7	0.00553	0.0062	0.0050	0.0060
0.75	0.024	0.030	0.024	0.023
0.8	0.020	0.030	0.020	0.022
0.85	0.038	0.069††		

* *Water in a glass tube 1 m. long and 6 cm. wide, examined in parallel light, measurements with bolometers.*

** *Water distilled twice in hard glass vessel, then placed in glass tube 50 cm. long, measurements with selenium barrier layer photocell.*

*** *Doubly distilled water in tube 100 cm. long lined with ceresin wax. Values computed from percentage absorption.*

† *In tube 100 cm. long lined with silver.*

†† *Taken from Dreisch's data.*

The absorption of light by salt solutions has received more attention by far than the absorption by pure water. Whereas only a few series of data are available for the passage of light through pure water, and the accuracy of the results is difficult to judge, hundreds of sets of determinations have been made on the absorption by water in lakes and oceans at different depths as well as in different seasons, and on its bearing on life under water (4). Everywhere the transparency of sea water increases during the transition from the coastal waters, influenced by rivers and waves, to the water of the continental slope with a depth of 0 to 1400 m. in the western North Atlantic, and to the open ocean. It is now well established that the most transparent water, in the Atlantic Ocean at least, absorbs only about ten times as much light, thickness for thickness, as the cleanest water ever tested in the laboratory (4). However, the absorption increases at the longer wave-lengths of the spectrum so that light in the region from 0.6 μ to the long wave-length limit of the visible range contributes little to the illumination at depths below the first few metres. This relatively slight absorption by the purest sea-water, in conjunction with the low sensitivity of the eye to the colours at both ends of the spectrum, is sufficient to extinguish the red below 15 m. depth, and to create the impression that, when seen from below, the surface of the ocean is a "slowly waving, pale green canopy" (2, p. 118). Orange vanishes below

50 m., yellow, at 105 m. At still greater depths there remains only a translucent black-blue, an illumination that has been called "stranger than any imagination could have conceived" by the first men to see it (2, p. 109, 119).

Although the extinction coefficient of unfiltered lake- and sea-water may seem to be large, it does not approach values comparable to those for opaque solid bodies, for instance, charcoal of the same thickness, except at wave-lengths in the near infrared (Table II). As pointed out many years ago by Aschkinass (1), if the small extinction coefficient in the middle part of the spectrum is set equal to unity, it increases to ten million for waves not even ten times longer, that is, near 3 μ, at the peak of one of the two fundamental vibration bands. Absorption of the same strength is found at the peak of the other band, near 6 μ. Beyond 6 μ, at any rate between 6.5 and 8.5 μ, the absorption remains at about the same level, the measurements giving an average value of 804 for the attenuation coefficient. Flames and incandescent bodies radiate the greater part of their energy in this region of the spectrum.

TABLE II

EXTINCTION COEFFICIENT k OF WATER IN BULK AT THE PEAKS OF THE INFRARED BANDS (14), ACCORDING TO THE FORMULA $I/I_0 = \epsilon^{-kz}$, AND AVERAGE ABSORPTION INDEX $n\kappa$ OF WATER, ACCORDING TO THE FORMULA $I/I_0 = \epsilon^{-4\pi\kappa nz/\lambda}$

Band wave-length, μ	Aschkinass	Jones	Collins	Dreisch	Suhrmann	Abs. index $n\kappa$
0.995	0.416	0.446	0.448	0.46	0.43	3.5×10^{-6}
1.21	1.221	1.297	1.22	1.30	1.205	1.2×10^{-5}
1.47	38.4		29.4	30.5	28.8	3.7×10^{-4}
1.97	123.2		103	104	108.2	1.7×10^{-3}
3.02	2733					0.065
6.09	2526					0.12
6.5 to 8.5	804					0.04 to 0.054

Less intense absorption bands are found at shorter wave-lengths, at 1.97, 1.47, 1.21, and 0.995 μ. Whereas a layer of water 1 cm. thick absorbs 38% of the radiation at $\lambda = 0.995\ \mu$, and 95% at 1.4 μ, a film of water only 10 μ, that is, $3\frac{1}{2}$ wave-lengths, thick, stops 9% of the radiation at 2.8 μ. When red and infrared light is contained in a beam illuminating spherical particles of small dimensions it is therefore necessary to ascertain, with the aid of Mie's theory, the influence of absorption upon the diffraction and the transmission of light.

Calculation of the Coefficient of Absorption

In the optical theory of absorption by solids or liquids, the coefficient of absorption κ in the index of absorption $n\kappa$, is referred to the thickness in wave-lengths measured in air rather than to the centimetre as is the custom in the laboratory, or to the metre, as is proper in studies of sea-water (Table II). The value of κ increases from the visible towards the infrared, from about

35×10^{-7} at the peak of the first absorption band, 0.995 μ, which is a harmonic of the fundamental frequency producing the band near 3 μ, to 3.7×10^{-4} at 1.47 μ, 0.04 at 3 μ, and 0.09 μ at the second fundamental vibration frequency near 6 μ. In the region between 6.5 and 8.5 μ its average value is 3/100 to 4/100. If κ is assumed to be 3/100, the region of strong absorption will be taken into account; the calculations will therefore in this study be carried out with $m = 4/3\ (1 - 3i/100)$ for the complex index of refraction of water.

The formula for the extinction coefficient k in the attenuation formula

$$\frac{I}{I_0} = \epsilon^{-kz}$$

representing the ratio between the intensity of the incident beam of light and that of the beam after it has travelled a distance z in air (refractive index $m_0 = 1$) containing in each unit N droplets of water of diameter $2a$, is the real portion of

$$k = \frac{\lambda^2}{2\pi m_0^2} Ni \sum_1^\infty (-1)^\nu (a_\nu - p_\nu),$$

so long as $N\pi a^2$, the total area of cross-section of the particles, is smaller than unity, that is, so long as there is no serious overlapping of the cross-sections. The symbols a_ν and p_ν designate the amplitudes of the different orders

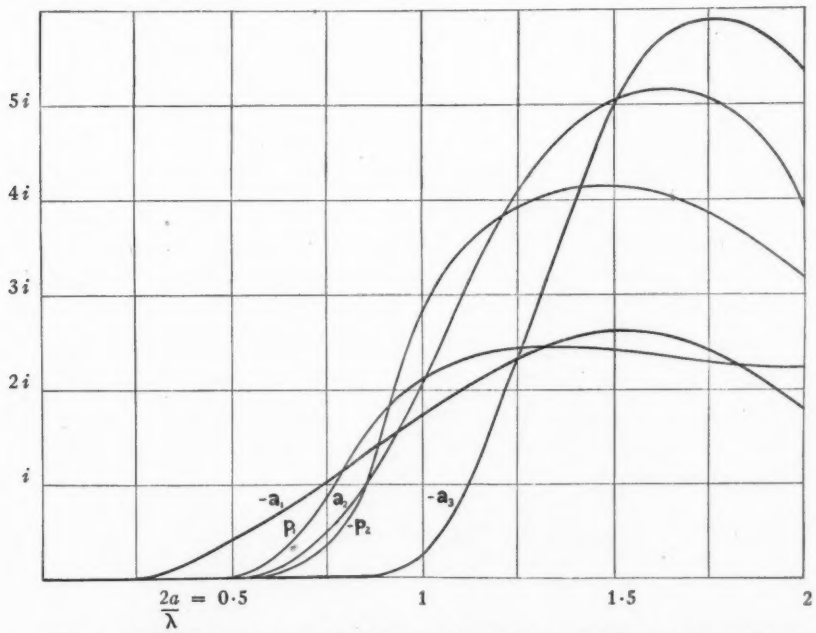

FIG. 1. *Amplitudes a_ν and p_ν of the electric and magnetic components of the oscillations issued by a spherical drop of water when it is exposed to a plane wave of unit amplitude and the fraction $2a/\lambda$ varies between 0 and 2 units.*

($\nu = 1, 2, 3$, etc.) of electrical and magnetic vibrations of the same frequency set up in a spherical particle by the incident light (Fig. 1). These amplitudes are given by expressions depending on Bessel functions J:

$$a_\nu = \frac{(-1)^\nu (2\nu + 1)}{-i + (-1)^\nu \dfrac{J_{-\nu-\frac{1}{2}}(\alpha)}{J_{\nu+\frac{1}{2}}(\alpha)} \dfrac{\dfrac{J'_{-\nu-\frac{1}{2}}(\alpha)}{J_{-\nu-\frac{1}{2}}(\alpha)} - \dfrac{\alpha}{\beta}\dfrac{J'_{\nu+\frac{1}{2}}(\beta)}{J_{\nu+\frac{1}{2}}(\beta)}}{\dfrac{J'_{\nu+\frac{1}{2}}(\alpha)}{J_{\nu+\frac{1}{2}}(\alpha)} - \dfrac{\alpha}{\beta}\dfrac{J'_{\nu+\frac{1}{2}}(\beta)}{J_{\nu+\frac{1}{2}}(\beta)}}}$$

$$p_\nu = \frac{(-1)^{\nu+1} (2\nu + 1)}{-i + (-1)^\nu \dfrac{J_{-\nu-\frac{1}{2}}(\alpha)}{J_{\nu+\frac{1}{2}}(\alpha)} \dfrac{\dfrac{J'_{-\nu-\frac{1}{2}}(\alpha)}{J_{-\nu-\frac{1}{2}}(\alpha)} - \dfrac{\beta}{\alpha}\dfrac{J'_{\nu+\frac{1}{2}}(\beta)}{J_{\nu+\frac{1}{2}}(\beta)}}{\dfrac{J'_{\nu+\frac{1}{2}}(\alpha)}{J_{\nu+\frac{1}{2}}(\alpha)} - \dfrac{\beta}{\alpha}\dfrac{J'_{\nu+\frac{1}{2}}(\beta)}{J_{\nu+\frac{1}{2}}(\beta)}}}$$

When $\alpha = 2\pi a/\lambda$, the derivatives of the Bessel functions of half-integral order obey the equations

$$\frac{J'_{\nu+\frac{1}{2}}(\alpha)}{J_{\nu+\frac{1}{2}}(\alpha)} = \frac{J_{\nu-\frac{1}{2}}(\alpha)}{J_{\nu+\frac{1}{2}}(\alpha)} - \frac{\nu}{\alpha}$$

$$\frac{J'_{-\nu-\frac{1}{2}}(\alpha)}{J_{-\nu+\frac{1}{2}}(\alpha)} = \frac{-J_{-\nu+\frac{1}{2}}(\alpha)}{J_{-\nu-\frac{1}{2}}(\alpha)} - \frac{\nu}{\alpha}.$$

The calculation of the ratios $J'(\beta)/J(\beta)$ is more cumbersome since $\beta = n(1 - i\kappa)\alpha$ is a complex quantity, but the recurrence equation

$$\frac{J'_{\nu+\frac{1}{2}}(\beta)}{J_{\nu+\frac{1}{2}}(\beta)} = \frac{1}{\dfrac{\nu}{\beta} - \dfrac{J'_{\nu-\frac{1}{2}}(\beta)}{J_{\nu-\frac{1}{2}}(\beta)}} - \frac{\nu}{\beta}$$

furnishes a useful check for the intermediate calculations required.

Discussion of Results

To express the results of the calculations, it is convenient again to define the coefficient of extinction in the formula for k in terms of unit surface rather than diameters, that is, to write

$$k = -2\pi a^2 K = -2\pi a^2 i \sum_1^\infty \frac{a_\nu - p_\nu}{\alpha^2}.$$

Here $2\pi a^2$ is the surface presented by the particle to the incident beam, whereas the real part of the sum depends on the expression $\alpha = 2\pi a/\lambda$ only.

A comparison of a series of values k_a and k, calculated with and without absorption, follows.

			k_a	k
For $2a/\lambda$ =	0.25	:	0.056	0.047
	0.5	:	0.19	0.19
	1.0	:	0.93	0.95
	1.5	:	1.515	1.7
(maximum)	2	:	1.7	1.95
	3.2	:		1.0

Despite the large value for the coefficient of extinction, the changes are so slight that in practice, except for work with infrared waves, they can be disregarded. Thus the main features of the absorption by perfectly transparent water remain unchanged, in particular, the rapid increase in absorption as the wave-length is decreased to the stage where it is equal to the radius. When the wave-length is halved, from eight times to four times the radius, the absorption is raised to a value at least four times as great, and when the wave-length is decreased once more in the same ratio, the absorption per unit area becomes five times as great as it was when the wave-length was equal to four times the radius. When the wave-length is reduced from a value equal to the diameter until it is equal to the radius, the increase is less rapid, particularly after the stage where $a/\lambda = 1/n$. A maximum is reached near the point where the wave-length is equal to the radius. From this stage onwards the absorption decreases when the wave-length is still further decreased and after one or a few fluctuations it reaches a constant value regardless of the wave-length (11).

When a fine mist, formed by water particles of the same radius, is illuminated by light of all frequencies, it will appear to have an absorption band that

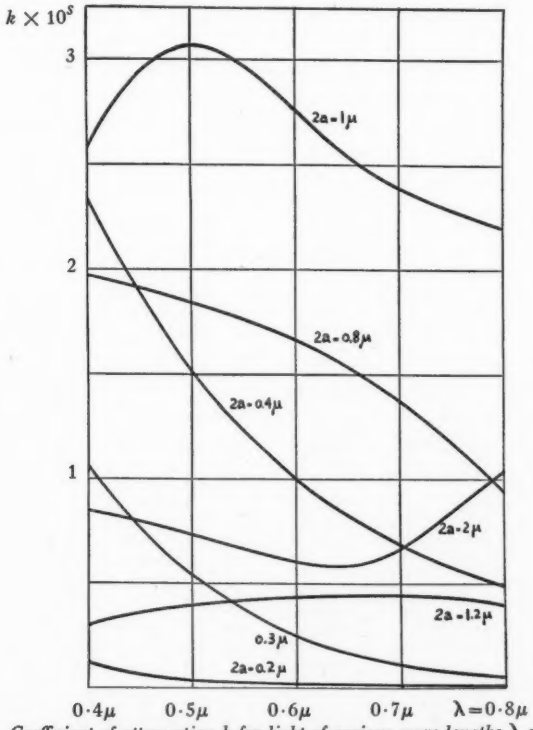

FIG. 2. *Coefficient of attenuation k for light of various wave-lengths λ and for water drops of different sizes (radius, a, between 0.1 and 2 μ). The exponent, s, is 10⁹ when 2a is between 0.2 and 0.5 μ, 10⁸ when 2a is between 0.5 and 1.0 μ, and 10⁷ when 2a exceeds 1 μ.*

reaches a peak where the wave-length is equal to the radius. If the radius of the particles is at the most equal to the shortest wave-length in the visible, the cloud will absorb most strongly in the blue and appear red in transmitted light. If, on the other hand, the radius of all the particles is equal to the longest visible wave-length, the particles will absorb most strongly in the red, and the cloud will appear green or blue in transmitted light (Fig. 2).

As regards the study of the growth of the particles, illuminated for this purpose by a strong light, assuming that the intensity of the scattered light is negligible, Mie's theory gives the following information on the colour changes to be expected. When the particles are so small that $2a/\lambda = 0.5$ for dark red light, this ratio will amount to 1.0 for the violet. Absorption in the violet is strong; in the red it is negligible, so that the droplets will appear to have an orange-red colour in transmitted light. After the particles have grown to twice their size, so that $2a/\lambda$ is equal to 1 for the red and equal to 2 for the violet, absorption in the blue remains predominant. With still larger particles the absorption is strong and fairly uniform for all wave-lengths. But when the ratios $2a/\lambda$ attain the value 2 for the red and about 4 for the violet, red and orange are most strongly attenuated by drops of this size, and the particles appear to possess a bluish-green colour. With further growth the colours fade more and more.

When the absorption of a given mass of water is considered, it is of course necessary to take into account the area presented by the drops to the incident light. The coefficient of extinction k in the attenuation formula is equal to $2\pi a^2 NK$, and since the total areas of particles are inversely proportional to the radius, increased dispersion of the material enhances the absorption of a given quantity of material.

References

1. ASCHKINASS, E. Ann. Physik (Ser. 3), 55 : 401-431. 1895.
2. BEEBE, W. Half mile down. Harcourt, Brace and Company, New York. 1934.
3. BLUMER, H. Z. Physik, 32 : 119-134. 1925; 38 : 304-328, 920-947. 1926; 39 : 195-214. 1926.
4. CLARKE, G. L. Sears Foundation, J. Mar. Research, 4(3) : 221-230. 1941.*
5. DREISCH, T. Z. Physik, 30 : 200-216. 1924.
6. LANGE, B. and SCHUSTERIUS, C. Z. physik. Chem. A, 159 : 303-305. 1932. (With correction in A, 160 : 468. 1932.)
7. MIE, G. Ann. Physik (Ser. 4), 25 : 377-445. 1908.
8. PARANJPE, G. R., NAIK, Y. G., and VAIDYA, P. B. Proc. Indian Acad. Sci. A, 9 : 333-351, 352-364. 1939.
9. POKROWSKI, G. I. Z. Physik, 43 : 394-403, 769-772. 1927.
10. RETTALIATA, J. T. Trans. Am. Soc. Mech. Engrs. 58 : 599-605. 1936.
11. SANDERSON, J. A. J. Optical Soc. Am. 30 : 405-409. 1940.
12. STODOLA, A. Steam and gas turbines. McGraw-Hill Book Company, New York. 1927.
13. STRATTON, J. A. and HOUGHTON, H. G. Phys. Rev. (Ser. 2) 38 : 159-165. 1931.
14. SUHRMANN, R. and BREYER, F. Z. physik. Chem. B, 20 : 17-53. 1933.
15. YELLOTT, J. I. Trans. Am. Soc. Mech. Engrs. 56 : 411-426; discussion, 427-430. 1934.
16. YELLOTT, J. I. and HOLLAND, C. K. Trans. Am. Soc. Mech. Engrs. 59 : 171-183; discussion, 507-510. 1937.

For earlier references see also R. Ruedy, Illumination and visual range under water. N.R.C. No. 1061. Ottawa, 1942.

Canadian Journal of Research

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOL. 21, SEC. B. OCTOBER, 1943 NUMBER 10

FROTH FLOTATION OF RUBBER AND RESIN COMPONENTS OF MILKWEED AND OTHER PLANTS THAT CONTAIN RESINS, RUBBER, BALATA, OR RELATED GUMMY SUBSTANCES[1]

BY WM. T. TURRALL[2], J. KLASSEN[3], AND H. SMEDLEY[2]

Abstract

Application of the froth flotation methods used in mineral dressing operations to the separation of rubber–resin fractions of milkweed offers hope of placing the extraction of such plant materials on a continuous rather than a batch basis. When the flotation method was used, no chemical treatment or flotation agents were necessary for the separation of rubber–resin from milkweed, though additional flotation reagents were found necessary for some other plants. The rubber–resin components of all plants studied, namely, milkweed, dogbane, goat's-beard, sow thistle, and wild lettuce, were successfully concentrated.

Under favourable conditions rubber–resins may not agglomerate during ball-milling; in some instances the flotation method can be used for the separation of the dispersed rubber–resin.

Introduction

Separation by froth flotation of rubber–resin components from milkweed *(Asclepias syriaca)* and other plants opens a new and simplified approach to the economic extraction of resins, rubber, balata, or related gummy substances. It is well known that there is an increasing interest and potential development in the realm of resins and plastic materials. What application this method of separation will have to the simplifying of their recovery can only be surmised at this time.

The use of froth flotation for such a separation applies the same principle in common use in mineral dressing operations. The pulp, consisting of prepared ground plant material and water, is subjected to agitation in a common type of mechanical or pneumatic flotation cell. Air is introduced into the pulp in the form of fine bubbles that attach themselves to the rubber–resin particles, and effect a concentration of this material at the top where it is removed as froth, designated as the concentrate. The remainder of the pulp containing only a small percentage of the rubber–resin fraction is rejected and is referred to as the tailings.

Various methods are being used for rubber–resin extraction from plants (1). In one method the plant material is subjected to alkali cooking, washing, and ball-milling, to form by agglomeration worms or balls of rubber and resin that

Manuscript received September 24, 1943.

Joint contribution from the Industrial Minerals Division of the Bureau of Mines, Ottawa, and the Division of Applied Biology of the National Research Laboratories, Ottawa. Issued as N.R.C. No. 1161.

[2] *Mining Engineer, Industrial Minerals Division of the Bureau of Mines.*

[3] *Chemical Engineer, Division of Applied Biology of the National Research Laboratories.*

can be recovered by screening. Such methods have hitherto been limited to batch operations, whereas it is believed that froth flotation, as a means of separating the rubber–resin fraction from the cellulose and inorganic matter, may make continuous operation possible.

In the investigational work froth flotation has been conducted mainly on common milkweed. To a limited extent dogbane (*Apocynum androsaemifolium* L.), goat's-beard (*Tragopogon pratensis* L.), sow thistle (*Sonchus arvensis* L.), and a wild lettuce, provisionally identified as *Lactuca spicata* (Lam.) Hitch., were also examined.

In the milkweed the rubber content varies from 1 to 4.5% and the resin content from 9 to 18% of the dry weight (1). The major components of the plant are carbohydrates (cellulose, etc.), fats, and proteins. The resins and hydrocarbons are believed to be stuck to the cell walls by proteins and other colloids. Liberation may be accomplished by a water or alkali cook to break down the proteins, etc., followed by fine grinding to complete the disintegration. The alkali cook has been considered essential, but investigational work has indicated it may not be necessary if froth flotation is used to concentrate the rubber–resin.

Preparation of Pulp

Different methods of preparation of pulp have been employed. The following example is one that has given satisfactory results with milkweed and has been used as the basis for the majority of these flotation tests.

Exactly 2.5 kg. of air-dry leaves is cooked under atmospheric pressure for three to four hours with 45 litres of a 1.5% caustic soda solution. This breaks down the proteins and saponifies the fats, rendering soluble approximately 60% of the dry weight of the leaves. The pulp is filtered and washed with either hot or cold water until the pH is in the range of 9.5 to 10. This may take from two to six hours but in a majority of cases four hours is sufficient. After thorough draining, the pulp consists of 1 part solids to 10 parts water. This pulp is pebble-milled for three to eight hours until the first minute worms of rubber are formed, when it is washed from the mill using about 4 litres of water. One-half litre of this pulp has been the standard charge used in a 600 gm. laboratory subaeration froth flotation machine. The percentage of solids in the pulp is about $1\frac{1}{4}$% of the total weight.

Froth Flotation

In all flotation tests it appeared advisable to float at a relatively low solid content. A solid content in the pulp exceeding 2% has presented difficulties that may be overcome in future test work, but in general it was found that the rubber–resin fraction contained more cellulosic matter at the higher density.

The flotation characteristics of this pulp are unique in that the pulp contains its own frothing and collecting reagents. No positive information has been established regarding the chemical identity of these reagents, but it is assumed

that they may be esters, alcohols, or fatty acids. Several tests have been made to improve both the grade and recovery of the rubber–resin concentrate by adding various flotation reagents having the properties of frothers, collectors, and frother-collectors. These have not produced a marked improvement but indicate that the use of some reagents may be advisable.

The frothing conditions in the cell vary with pulp preparation. In all cases a very stable wet froth is obtained. If the pulp has had an alkali cook a medium sized bubble results. Pulp that receives a water cook produces only very large bubbles, whereas uncooked pulp produces voluminous froth composed of very fine bubbles. Though slight frothing persists on the removal of the concentrate, tests show that the majority of the rubber–resin fraction has been removed. Although not definitely proved, it is assumed that much of the remaining rubber–resin in the pulp is still entrapped within the cell tissue or agglomerated into worms too large to float (see Table II). If so, increased recoveries would be difficult to obtain without a modification of the preliminary treatment.

Few difficulties were encountered in the froth flotation separation and results indicate that this method may be of commercial importance. It should be realized, however, that much further work is necessary to establish proper conditions before ultimate grade and recovery can be obtained.

The results of a test on milkweed leaves with no flotation reagents added are shown in Table I.

TABLE I

FLOTATION OF RUBBER–RESIN COMPONENTS FROM MILKWEED—NO REAGENTS, RUBBER AGGLOMERATIONS VISIBLE

Product	Weight, %	Analyses, %		Distribution, %	
		Acetone extract (resins)	Benzene extract (rubber)	Acetone extract (resins)	Benzene extract (rubber)
Concentrate	24	23.0	13.5	56	75
Tailings	76	5.56	1.37	44	25
Calculated feed	100	9.67	4.22	100	100

In the tests recorded above, the ball-mill operation was stopped when the rubber particles had agglomerated until barely visible to the naked eye.

In the test reported in Table II similar flotation conditions prevailed, but the pulp in this case had been subjected to ball-milling operations until the rubber particles had agglomerated and some had reached the size of 2 to 3 mm. in length. The recovery of the rubber–resin components under such conditions is decidedly lower.

TABLE II

FLOTATION OF RUBBER–RESIN COMPONENTS FROM MILKWEED—NO REAGENTS, RUBBER AGGLOMERATED

Product	Weight, %	Analyses, %		Distribution, %	
		Acetone extract (resins)	Benzene extract (rubber)	Acetone extract (resins)	Benzene extract (rubber)
Concentrate	20	25.1	8.2	40.5	50.6
Tailings	80	9.3	2.0	59.5	49.4
Calculated feed	100	12.5	3.3	100.0	100.0

Agglomeration takes place during the ball-milling only when conditions of density and alkalinity are favourable. Under unfavourable conditions the rubber is so well dispersed through the pulp that it stubbornly resists agglomeration. The concentrate obtained by flotation yielded a good recovery of rubber on further treatment. The results of a test under such conditions are shown in Table III.

TABLE III

FLOTATION OF RUBBER–RESIN COMPONENTS FROM AN EMULSIFIED PULP

Product	Weight, %	Analyses, %		Distribution, %	
		Acetone extract (resins)	Benzene extract (rubber)	Acetone extract (resins)	Benzene extract (rubber)
Concentrate	24.3	16.90	5.67	72.3	82.2
Tailings	75.7	2.09	0.40	27.7	17.8
Calculated feed	100.0	5.69	1.68	100.0	100.0

The effect of various flotation reagents in the separation of the rubber–resin constituents are summarized in Table IV.

TABLE IV

COMPARISON OF FLOTATION GRADES WITH AND WITHOUT FLOTATION REAGENTS

Reagent	Analyses, %			
	Acetone extract (resins)		Benzene extract (rubber)	
	Concentrate	Tailings	Concentrate	Tailings
None	24.3	10.6	13.2	4.3
Oleic acid	24.0	9.7	13.3	5.3
A.C. 708	23.9	8.8	14.0	4.8
Orso	22.9	8.7	14.8	3.6
B-23	23.2	8.2	14.0	3.5
Frother 60	23.3	9.7	14.4	3.7
Pine oil	24.3	9.1	12.9	3.6

The milkweed leaf used in this particular series of experiments was from an early July collection, at which time a suitable rubber–resin fraction had not been developed. These tests do, however, show a comparison of the grade of the products obtained with and without flotation reagents.

Table V shows the relation of the time of grind to the grade and the recovery of the rubber and resins. No alkali cook was used in the preliminary treatment.

TABLE V

EFFECT OF TIME OF GRIND ON GRADE AND RECOVERY BEFORE AGGLOMERATION

Time of milling, hr.	Product	Weight, %	Analyses, %		Distribution, %	
			Acetone extract (resins)	Benzene extract (rubber)	Acetone extract (resins)	Benzene extract (rubber)
2	Concentrate	21	21.1	5.2	39	45
	Tailings	79	8.9	1.7	61	55
	Calculated feed	100	11.5	2.4	100	100
4	Concentrate	23	21.0	5.7	45	53
	Tailings	77	7.6	1.5	55	47
	Calculated feed	100	10.7	2.5	100	100
6	Concentrate	22	21.6	6.1	47	58
	Tailings	78	6.7	1.2	53	42
	Calculated feed	100	9.9	2.3	100	100

The above results seem to indicate that a greater percentage of the resins and rubber are being liberated and concentrated on increased grinding.

Investigational work conducted on the other named plants was done in a similar manner and the results of flotation tests are shown in Tables VI and VII.

TABLE VI

FLOTATION TESTS ON DOGBANE, GOAT'S-BEARD, AND WILD LETTUCE WITH AN ALKALI COOK (1.5% CAUSTIC SODA)

Material	Product	Weight, %	Analyses, %		Distribution, %	
			Acetone extract (resins)	Benzene extract (rubber)	Acetone extract (resins)	Benzene extract (rubber)
Dogbane*	Concentrate	11.8	35.6	14.4	38.4	63.2
	Tailings	88.2	7.6	1.12	61.6	36.8
	Calculated feed	100.0	10.9	2.69	100.0	100.0
Goat's-beard	Concentrate	17.9	27.9	3.13	82.9	83.5
	Tailings	82.1	1.26	0.13	17.1	16.5
	Calculated feed	100.0	6.03	0.67	100.0	100.0
Lactuca	Concentrate	35.2	22.8	3.51	85.3	91.0
	Tailings	64.8	2.14	0.19	14.7	9.0
	Calculated feed	100.0	9.43	1.36	100.0	100.0

* *An agglomerated ball of rubber and resins was removed from the pulp before flotation.*

TABLE VII

FLOTATION TESTS ON DOGBANE, GOAT'S-BEARD, SOW THISTLE, AND WILD LETTUCE WITH A WATER COOK ONLY

Material	Product	Weight, %	Analyses, %		Distribution, %	
			Acetone extract (resins)	Benzene extract (rubber)	Acetone extract (resins)	Benzene extract (rubber)
Dogbane	Concentrate	30.4	37.6	12.96	80.0	91.8
	Tailings	69.6	4.12	0.50	20.0	8.2
	Calculated feed	100.0	14.31	4.29	100.0	100.0
Goat's-beard	Concentrate	4.4	20.7	1.49	40.9	49.6
	Tailings	95.6	1.38	0.07	59.1	50.4
	Calculated feed	100.0	2.23	0.13	100.0	100.0
Sow thistle	Concentrate	48.1	11.62	1.47	86.0	85.6
	Tailings	51.9	1.76	0.23	14.0	14.4
	Calculated feed	100.0	6.51	0.83	100.0	100.0
Lactuca	Concentrate	10.5	23.86	2.24	59.6	60.8
	Tailings	89.5	1.90	0.17	40.4	39.2
	Calculated feed	100.0	4.21	0.39	100.0	100.0

Summary

Some of the more important features of froth flotation in the separation of rubber–resin from milkweed and other plants are summarized as follows:

1. It removes the bulk of the waste material at an early stage of the operation.

2. In the flotation of the rubber–resin component from milkweed, no additional flotation reagents are needed to cause a separation but they have been found necessary in the flotation treatment of some other plants.

3. The grade and the recovery of the rubber–resin fractions appear to depend on the size of the agglomerates.

4. Agglomeration of the rubber–resin fraction takes place during ball-milling only when certain conditions are favourable, e.g., density and alkalinity. If conditions are not favourable the rubber–resin remains fine and well dispersed. Flotation on such a product results in the separation of a rubber–resin fraction.

5. It is not necessary to take the specific gravity of the rubber–resin constituents into consideration.

6. The flotation method is applicable to the concentration of the rubber–resin components from such plants as milkweed, dogbane, goat's-beard, sow thistle, wild lettuce, and possibly many other plants with or without the use of chemicals.

7. It presents the possibility of a continuous process of rubber–resin extraction from plants.

Acknowledgments

The writers' thanks are due to Dr. N. H. Grace of the National Research Laboratories for encouragement, advice, and helpful suggestions. Thanks are also due to Mr. N. Levitin, Laboratory Assistant, and to Miss E. Hornell and Mr. G. D. Powers, Laboratory Helpers, National Research Laboratories, for valuable technical assistance.

Reference

1. GRACE, N. H., WATSON, R. W., and KLASSEN, J. Can. J. Research. In press.

THE PHYSICAL STATES OF ANHYDROUS SODIUM SOAPS[1]

By Wilfred Gallay[2] and Ira E. Puddington[2]

Abstract

Density measurements and differential cooling curves have been carried out on sodium stearate and sodium oleate over a range of temperatures. For sodium stearate, the genotypical or unidimensional melting point at 70° C. found by Thiessen *et al.* has been corroborated. A large transition has been noted at about 100° C. and it is suggested that this phase transition is due to a melting in a second dimension at right angles to the molecular axis. A further large transition has been found at 125° to 130° C. leading to a plastic state in the soap, and it is suggested that this transition point denotes the essential completion of bidimensional melting of the lattice. No further considerable phase change was found up to about 200° C., when disruption of the polar bonds probably occurs to effect complete disruption of the lattice to the liquid crystalline state. Only the latter transition point was found for sodium oleate at about 135° C.

The sodium soaps are relatively readily crystallizable materials, several of which have been obtained in the form of single crystals and submitted to X-ray analysis. Sodium stearate has, for example, been particularly extensively investigated in this regard, and has been shown to consist of soap molecules arranged in a well-ordered lattice. The lattice constants in the three dimensions are well known and it has been demonstrated (6) that the length of the identity period along the direction of the axis of the molecules corresponds to a double molecule, with due allowance for the angle of inclination to the basis plane. A crystallite of sodium stearate consists therefore of a large number of molecules parallel to one another and all at a definite angle to the crystal axis; the molecules are arranged in planes in such a manner that along their axes two adjacent sodium carboxylic groupings and two adjacent methyl groups alternate between the molecules.

Since the soap molecule is distinctly heteropolar, it is apparent that the forces holding the lattice together are of two types, viz., (i) polar bonds between the strongly polar sodium carboxylic groups, and (ii) non-polar bonds between adjacent hydrocarbon chains, corresponding to Van der Waal's forces. That the polar bonds are tremendously stronger than the non-polar bonds is strikingly shown by the difference in melting points among soap, fatty acid, and hydrocarbon of corresponding chain length. The introduction of the carboxyl group into the 18 carbon chain raises the melting point from 28° to 70° C., and the further substitution of the sodium to form the soap raises the melting point to about 200° C., where a liquid crystal state is attained. Different metallic ions may be expected to show different effects and this is reflected in the melting points of the corresponding soaps. The magnitude of the non-polar bond should increase with length of hydrocarbon chain and eventually exert a considerable influence on the ease of

[1] *Manuscript received August 3, 1943.*

Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1158.

[2] *Chemist.*

dissolution of the polar bonds. This is apparent from consideration of the solubility in water of sodium salts of straight chain aliphatic acids. The higher members of this series show only a very slight solubility in water.

The effect of heat on a crystal of sodium stearate is of particular interest. It has been shown (5) that a monotropic alteration occurs in the crystal at about 50° C., leading to a more stable form, but this is of minor significance only in a general consideration of the reversible transitions in physical state with temperature. During the temperature interval up to 70° C., the hydrocarbon chains of the fatty acid or soap attain increased energy of rotation about the freely rotatable C–C linkages.

Stearic acid itself melts at about 70° C., at which point sufficient energy has been provided for a complete disruption of the cohesional forces not only between the hydrocarbon chains but also between the polar bonds. In the case of sodium stearate, the orienting effect of the highly polar grouping undoubtedly assists in maintaining the mean position of the hydrocarbon chains. The empirical rule of Krafft, postulated many years ago, states that in aqueous soap sols a sudden change in the state of dispersion of the soap takes place on cooling to the melting point of the fatty acid corresponding to the soap. This change has been variously ascribed to alterations in solubility and to crystal growth.

More recently, Thiessen and his co-workers (2, 3) have shown that the empirical rule of Krafft is actually borne out by precise measurements and that a form of melting is involved. This conclusion was reached by the consideration of such evidence as the following. The value of the optical double refraction in a single crystal of sodium stearate remains constant up to about 70° C., and then decreases continuously. The interferences representing the larger spacing at right angles to the molecular axis broaden out at 70° C. (4), indicating an increasing amplitude of oscillation in that direction. A curve of specific volume versus temperature shows a small but distinct break at 70° C. The specific heat and dielectric constant also show irregularities at this point. These authors conclude therefore that a unidimensional melting occurs at 70° C., i.e., sufficient thermal energy has been provided to bring about a loosening of the lattice in one dimension. Because of the relation to the melting point of the corresponding fatty acid, this was termed the genotypical point.

It is apparent that a wide range of temperature remains above 70° C. before complete melting occurs, in which other changes in physical state may take place. Lawrence (1) states that there is no break in the density–temperature curve until a temperature of about 220° C. is reached, although he notes a transition from a "hard fully-crystalline state" to a "soft-crystalline state" at 163° C. In general, the measurements of Thiessen were carried up to only several degrees above the genotypical point.

In the present work, the characteristic of density was chosen first for investigation as to changes in physical states of soaps on heating. The method used precluded errors due to occlusion of air and is suitable for use

over a wide range of temperatures. Fig. 1 shows results obtained with four sodium stearates of varying origin and degree of purity. The differences in density obtained between Curves 1 and 2 are typical of many others noted in repeat experiments, and are very likely due to vacuoles in the melted and cooled soap blocks under measurement.

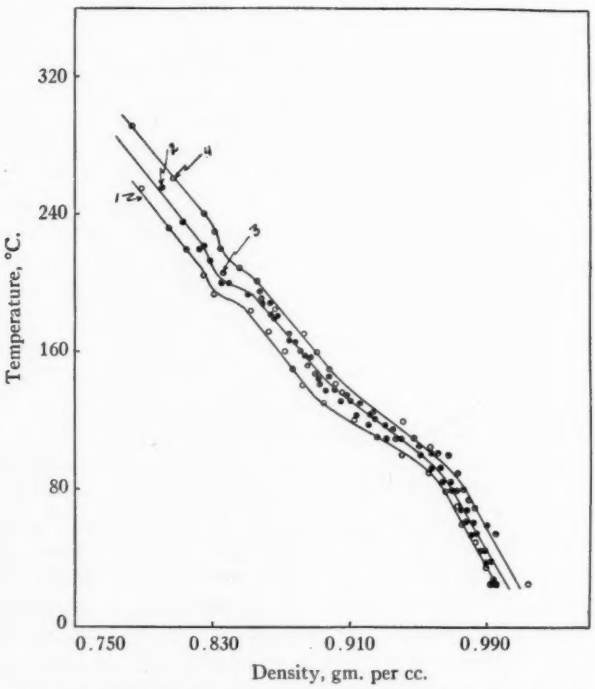

FIG. 1. *Density–temperature relation for sodium stearate. 1 and 2, Laboratory prepared, carefully purified; 3, Schuchardt's product; 4, technical grade.*

It is noted that the forms of these curves, particularly of the first three, are virtually identical. An initial linearity is obtained up to a temperature of about 70° C. Above this temperature, the density falls off more rapidly until a temperature of about 125° to 130° C. has been reached. Above this point, the density again decreases essentially linearly with increase in temperature up to about 190° C. There is then found a sudden greater decrease in density over a short interval followed by another brief interval of a lesser decrease in density to 210° C. Following this, the density again decreases linearly with the temperature. The technical soap shows an appreciably higher melting point, due possibly to the presence of appreciable quantities of lower molecular weight fatty acids.

These curves are of particular interest in the matter of the physical state of the soap. The genotypical point of Thiessen requires a break in the curve at 70° C., and Fig. 2 shows his dilatometric results indicating a sharp change in direction at this temperature. In the present work, a number of density

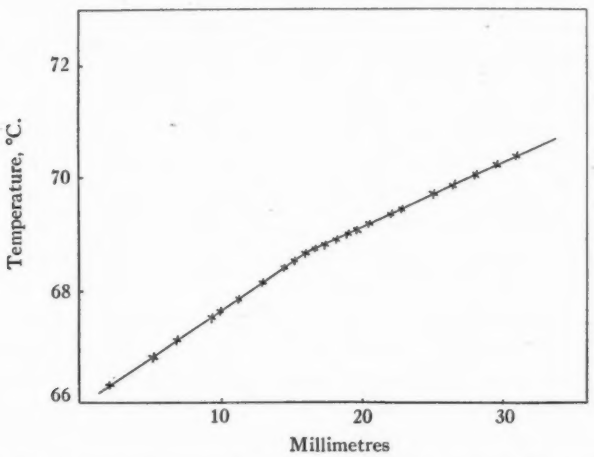

FIG. 2. *Dilatometric results of Thiessen and Ehrlich, showing the genotypical point for sodium stearate.*

determinations were made in this region and the results are shown in Fig. 3. It is noted that a definite departure from linearity occurs at about 70° C., but the curvature continues at higher temperatures. The increase in volume with temperature is particularly marked in the region from 105° to 125° C.

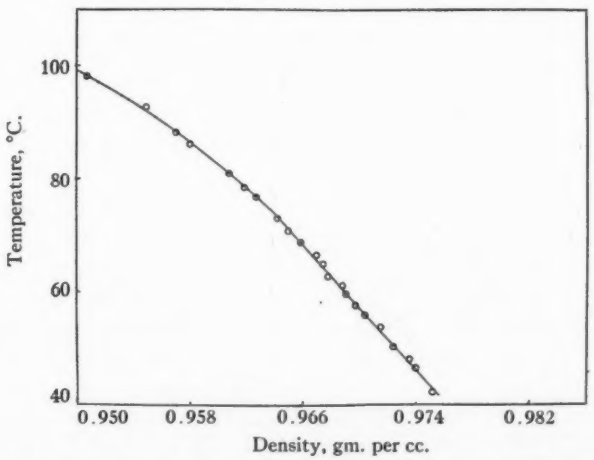

FIG. 3. *Density–temperature relation for sodium stearate, in detail up to 100° C.*

The writers have corroborated therefore the observation of unidimensional melting at 70° C. The increase in volume is relatively small. The hydrocarbon chains are now oscillating in one dimension, thus wiping out one lattice dimension where the larger spacing indicates the weaker cohesional bond. As the temperature is raised, further thermal energy is provided and the amplitude of the vibration increases, giving rise to an increased specific volume. At a higher temperature it may be expected that vibration can begin in a second dimension at right angles to the molecular axis, and the hydrocarbon chains can then describe a skipping rope type of motion.

That a break actually occurs at about 100° C. was found by carrying out a differential cooling curve on a sample of pure sodium stearate. The results of duplicate experiments are shown in Fig. 4. A relatively sharp discontinuity is noted at about 100° C., showing definitely that heat is given off at this temperature owing to a partial solidification. It is apparent that there should be a break also at 70° C., but this change is so slight compared with that at 100° C. that the writers' method of procedure was not capable of showing this very small deflection. The relative magnitudes are shown also in the density–temperature curves of Fig. 1. It is suggested therefore that a bidimensional melting point for sodium stearate is reached at about 100° C., involving a loosening of the lattice in the smaller of the two sideways spacings of the lattice.

The density continues to decrease rapidly above 100° C. until a temperature of about 125° to 130° C. is reached, where a further change is noted in the density–temperature curve. Fig. 4 shows a second distinct break in the

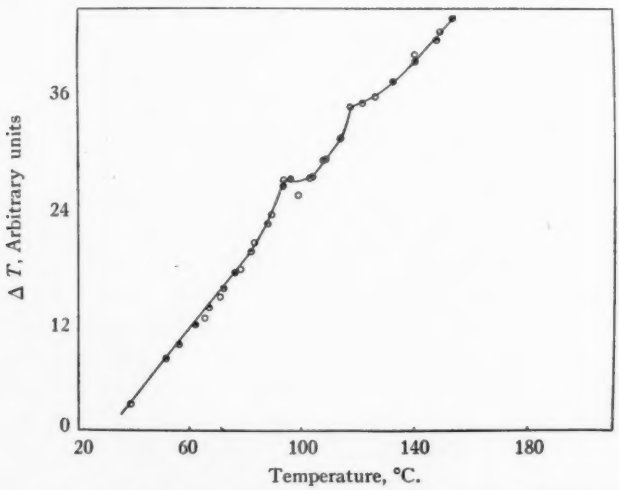

FIG. 4. *Differential cooling curve for sodium stearate, in duplicate.*

differential cooling curve at this temperature, denoting a sharp physical change in the soap. If a sample of the soap is heated in a test-tube, it is found that the soap becomes plastic quite suddenly at about 125° C., as judged from its tendency to smear. It has been noted (2) that the value for the double refraction becomes zero at about 130° C. At this temperature (125° to 130° C.), the hydrocarbon chains have probably attained a maximum freedom of motion in two dimensions. The polar bonds holding the soap molecules together are not appreciably affected in view of their very high strength. We may refer to 125° to 130° C. as the plasticity point of sodium stearate. The lattice constant corresponding to the double molecular length is probably unchanged. It might be expected that such a material would be plastic, since plastic systems require some medium for slip or deformation of the system, and it is quite probable that this medium is afforded by the "melted" portions of the lattice. At this stage, the soap can be drawn out into long threads which are highly birefringent.

This sharp transition point, denoting the relatively complete loosening of the lattice in a second dimension, is further shown in the fact that a sodium stearate suspension in a mineral oil shows a sudden considerable increase in viscosity at about 120° C. This "swelling temperature" is the same for oils of both high and low viscosity index, since the transition is due to thermal energy in the soap lattice rather than to solvent action of the oil. The plastic nature of the partially melted soap crystals probably leads to an interlacing or sticking on surfaces, which contributes further to an increase of viscosity. At this state, if a glass needle be drawn over a sample of soap suspension in oil on a microscope slide, it may be seen that the applied stress brings about the movement of a large mass of the suspension over most of the area relatively far removed from the needle.

The density–temperature relation between 125° and 190° C. shows no marked irregularities and it is probable that any changes in physical state in this region are of minor significance. The density decreases steadily owing to the greater volume encompassed by the rotational and translational movements of the non-polar hydrocarbon chains. The coefficient of thermal expansion in the plastic state is somewhat greater than in the crystalline state as might be expected.

At about 190° C., there is observed a large increase in specific volume followed by a brief interval of smaller change in density. Linearity is again attained at about 210° C. A large reduction in viscosity is observed visually, and it is apparent that a drastic melting has occurred. It is probable that at this stage, sufficient energy has been provided for the disruption of the polar bonds in the lattice, to a liquid crystal state of the soap. The melting point is somewhat higher, about 240° C., for the technical sodium stearate. The shape of the curve in the region of this melting to a liquid crystalline condition appears to indicate that the liquid has a higher density than the partially melted plastic soap, and this was actually proved experimentally.

Since this work was carried out (1939), Vold, Macomber, and Vold (7) have described dilatometric measurements on anhydrous sodium stearate over a range of temperatures, and have shown irregularities in the volume–temperature curve, which in some instances were confirmed by microscopic observation using a special technique. Between room temperature and the liquid–crystalline condition, the following transition temperatures were found by them: 90°, 117°, 132°, 167°, 198° to 205° C. Examination of the curve shows that the results obtained by these workers are not substantially different from those found in the present work. It is noted that they obtain two large irregularities, one ranging from 120° to 130° C., corresponding to the writers' plasticity point, and one from 190° to 200° C., corresponding to the writers' three-dimensional melting point. There is a gradual curvature up to about 130° C. The inferred breaks at 90°, 117°, and 167° C. are small, and only the last named of the three obtained any confirmation by the hot-stage technique.

Fig. 5 shows the density–temperature relation for commercial neutral sodium oleate and laboratory prepared pure neutral sodium oleate. It is noted that the relation is essentially linear up to about 100° C., when the rate of density decrease changes. Linearity is again attained at about 135° to 140° C. It

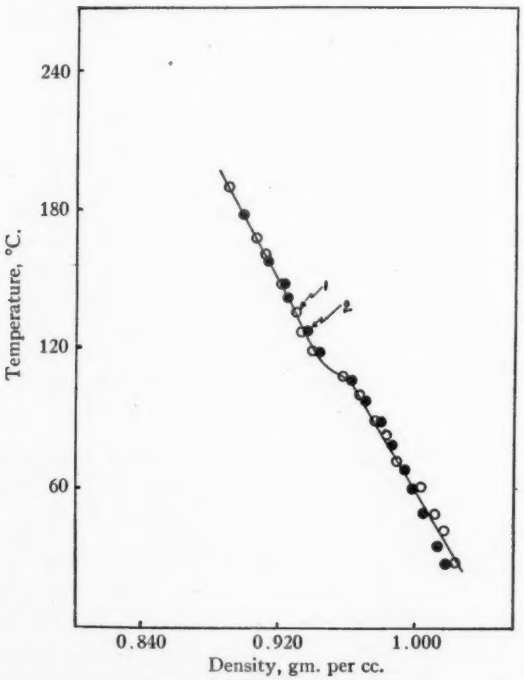

FIG. 5. *Density–temperature relation for sodium oleate. 1, Commercial neutral grade; 2, laboratory prepared, carefully purified grade.*

is apparent that this temperature represents the full or three-dimensional melting point of the crystal of sodium oleate. There is of course no genotypical point within the temperature range investigated. These results show some points of similarity with those obtained for sodium oleate by Vold, Macomber, and Vold (7, p. 174). The break that they obtained at 68° C. is very small and might well be due to experimental error. Their curve shows also a break in density between about 115° and 135° C., which corresponds roughly to the main change in the writers' Fig. 5. In the present work, no indication was obtained of any change in physical state corresponding to their figure of 169° C.

Experimental

Density Measurement.—The soap powder was melted under vacuum to a solid block. This block was then placed in a glass tube of slightly greater dimension, the closed end of which was fitted with a small glass hook. Constrictions in the tube were then made in order to keep the block in place. The tube was drawn down and the pycnometer completed by sealing on a length of capillary tubing and bending to a U-form. Mercury was added under vacuum. The weight of the soap used was known and the volume of the soap at room temperature was previously determined separately by a buoyancy method involving displacement of mercury. The pycnometer was exposed to various temperatures in an air-bath consisting of a heavily insulated vessel fitted with well distributed heating coil, regulator, and high-speed stirrer. Temperature could be controlled to within $\pm$ 0.25° C. A new pycnometer was constructed for each system investigated.

Differential Cooling.—The soap was melted in a small magnesium block, which in turn was placed in a heavy-walled brass cylinder immersed in a bath of aluminium turnings. Two thermocouples were fitted to this apparatus, viz., (i) in a glass tube immersed directly in the soap and (ii) inserted in a hole in the wall of the magnesium block. No. 2 thermocouple was attached in the usual way to a sensitive galvanometer with mirror and scale, so that the hot junction was in the soap and the cold junction in the magnesium block. The whole arrangement was heated and allowed to cool, and the temperature differential between the soap and the wall was measured in relation to the temperature of the soap itself. A number of readings were taken over a range of temperatures as the system cooled.

Acknowledgment

This work was carried out under an arrangement between the Imperial Oil Limited and the National Research Council.

The authors wish to express their thanks to Imperial Oil Limited for permission to publish this paper.

References

1. LAWRENCE, A. S. C. Trans. Faraday Soc. 34 : 660-677. 1938.
2. THIESSEN, P. A. and EHRLICH, E. Z. physik. Chem. A, 165 : 453-463. 1933.
3. THIESSEN, P. A. and KLENCK, J. v. Z. physik. Chem. A, 174 : 335-358. 1935.
4. THIESSEN, P. A. and SPYCHALSKI, R. Z. physik. Chem. A, 156 : 435-456. 1931.
5. THIESSEN, P. A. and STAUFF, J. Z. physik. Chem. A, 176 : 397-429. 1936.
6. THIESSEN, P. A., STAUFF, J., and WITTSTADT, W. Angew. Chem. 49 : 640-642. 1936.
7. VOLD, M. J., MACOMBER, M., and VOLD, R. D. J. Am. Chem. Soc. 63 : 168-175. 1941.

THE EFFECT OF CERTAIN ADDITION AGENTS ON THE PHYSICAL STATES OF SODIUM SOAPS[1]

By Wilfred Gallay[2] and Ira E. Puddington[2]

Abstract

The effect of glycerol and of polar and non-polar mineral oils on the density–temperature relations of sodium stearate and sodium oleate have been measured. A non-polar solvent such as a high V.I. oil has no effect, and may be regarded as an inert diluent. Glycerol and low V.I. oils have similar effects on the physical states of the soap. Up to the unidimensional melting point of the soap, the polar solvents have no effect. Above this point, however, an increasing effect is obtained both with increase in temperature and with amount of solvent. The effect is particularly marked above the plasticity point but may be large also in the region of the bidimensional melting point of the soap. The orienting effect of the non-polar hydrocarbon chain on the polar grouping of the soap in the presence of a polar solvent is discussed. The influence of excess acid and alkali in the soap is described.

In view of the distinctive bipolar character of a sodium soap, consisting of a highly polar sodium carboxylic grouping and a non-polar hydrocarbon chain, addition agents may be classified as to polarity in their effect on the physical state of the soap. The effect of polar compounds would be exerted solely on the polar bonds in the soap lattice and the effect of non-polar compounds would be exerted on the non-polar bonds between hydrocarbon chains. The length of the hydrocarbon chain is obviously of importance, as shown by the decreasing solubility in water of sodium salts of straight chain aliphatic acids, with increasing molecular weight of the acid.

A previous communication (1) dealt with phase transitions in sodium soaps. The present work deals mainly with the effect of glycerol and mineral oils on the physical states of the soaps. These addition agents were chosen in view of their importance in lubricating greases; this work presents data obtained during an extensive investigation of such systems.

Fig. 1 shows the density–temperature relations for neutral technical sodium stearate alone and with addition of various quantities of glycerol. It is noted that linearity is maintained up to the genotypical point at 70° C., followed by a gradually increasing specific volume up to about 130° C. All the curves show a sharp transition at 130° C., but the effect of the glycerol then becomes marked. The sharp transition of complete melting to a liquid crystal state at about 200° C. (1) is completely absent, and it is obvious from visual examination that the soap is completely melted at temperatures far below the melting point of the soap alone.

[1] *Manuscript received August 3, 1943.*
Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1159.
[2] *Chemist.*

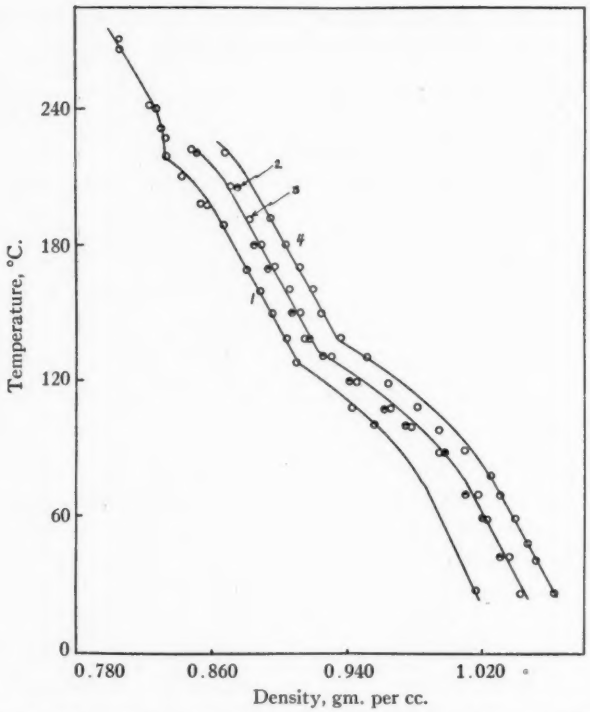

FIG. 1. *Effect of glycerol on the density–temperature relation of sodium stearate. 1, Neutral technical sodium stearate alone; 2, with 4.7% of glycerol; 3, with 8.7% of glycerol; 4, with 19.1% of glycerol.*

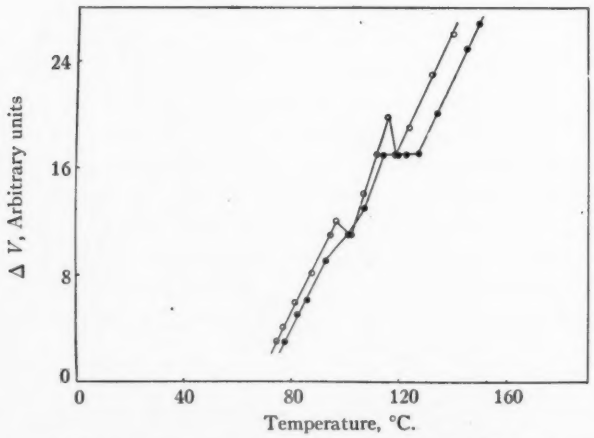

FIG. 2. *Differential cooling curves on sodium stearate with 20% of glycerol, in duplicate.*

Differential cooling curves on sodium stearate containing 20% glycerol were measured and the results of duplicate measurements are shown in Fig. 2. Breaks in the curves are shown at about 100° and 125° C. These correspond to transition points shown by the soap alone (1).

Fig. 3 shows the density–temperature relations for an alkaline sodium stearate containing 2.5% of free alkali, alone and with various quantities of glycerol. The results are similar to those obtained for the neutral soap

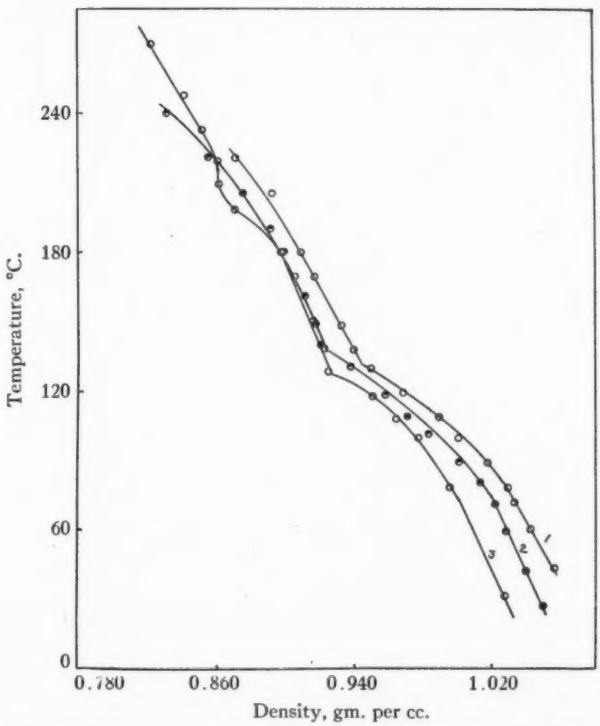

FIG. 3. *Effect of glycerol on the density–temperature relation of alkaline sodium stearate. 3, Alkaline sodium stearate (2.5% of free alkali) alone; 2, with 2% of glycerol; 1, with 7.5% of glycerol.*

with glycerol admixtures. The effect of the glycerol is obtained above the plasticity point (125° to 130° C.), and the melting point of the soap is greatly decreased.

Fig. 4 shows the density–temperature relations for a system containing sodium stearate and various mineral oils. These mineral oils varied in polarity as judged from the viscosity index values. No appreciable change was produced by the addition of a high V.I. oil. The measurements were

extended only up to about 200° C., owing to the relatively high vapour pressure of the oil, but no indications of melting or solution of the soap were obtained at lower temperatures.

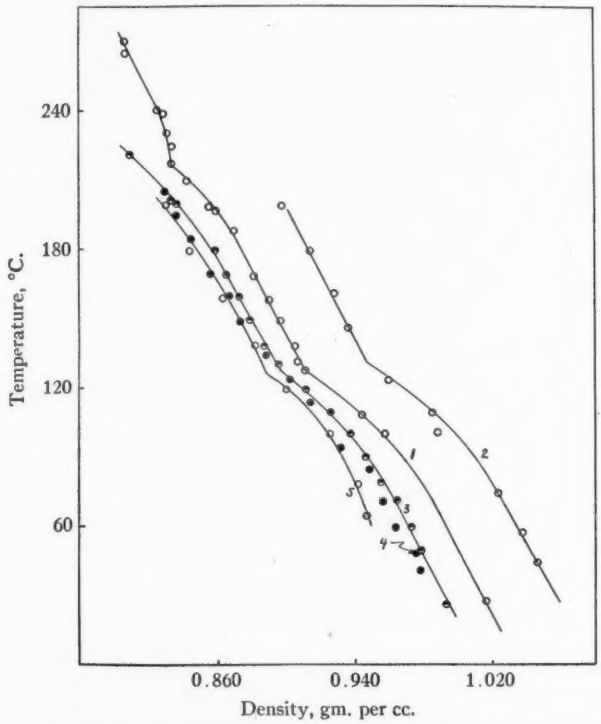

FIG. 4. *Effect of mineral oil on the density–temperature relation of sodium stearate. 1, Neutral technical sodium stearate alone; 2*, with 23.5% of a non-polar oil (900 vis., 95 V.I.); 3, with 23.5% of a polar oil (900 vis., 40 V.I.); 4, with 38% of a polar oil; 5, with 68% of a polar oil.*

* *This curve displaced for clarity by adding 0.06 to all density values.*

The effect of an oil of much greater polarity (40 V.I.) is however markedly different. Three of the curves in Fig. 4 show the results for additions of various quantities of 900 vis. 40 V.I. oil. The absolute values for the densities are of course lowered by the oil. The curves have much the same form as that for the soap alone. Analogous to the case of glycerol, in Curve 3 there is no effect on the soap until the plasticity point is reached at about 125° to 130° C. Above this point, a gradual melting or solution occurs. The melting point is lowered according to the amount of polar oil available. In Curve 5, with 68% of the polar oil, there is little evidence of sharpness of phase change at the plasticity point and actually, from visual observation, the mixture appeared homogeneous at about 110° C. The neutralization number of this

oil is 0.28, which is appreciably larger than the free acid content of the oil of high viscosity index. By comparison with Fig. 6, it is seen however that these small quantities of free acids can have no significant effect on the physical state of the soap until the region of complete melting is approached. The effect obtained with the polar oil is therefore to be ascribed to the chemical nature of the oil constituents and not to the small amounts of free fatty acid contained.

Fig. 5 shows similar results obtained with sodium oleate, alone and with various amounts of 900 vis. 40 V.I. oil. It is noted that the phase change representing the complete melting point (135° to 140° C.) is gradually

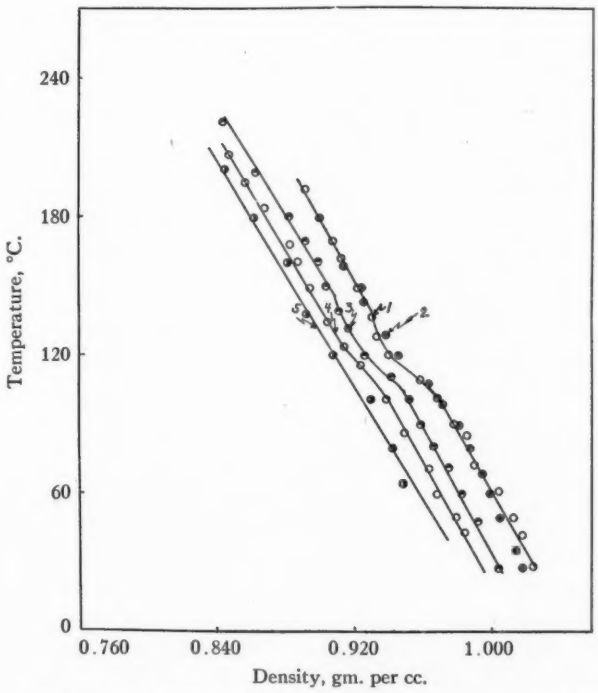

FIG. 5. *Effect of mineral oil on the density–temperature relation of sodium oleate. 1, Commercial neutral sodium oleate alone; 2, laboratory prepared neutral sodium oleate alone; 3, with 17% of a polar oil (900 vis., 40 V.I.); 4, with 30% of a polar oil; 5, with 62% of a polar oil.*

washed out, until with large quantities of polar oil, no definite melting point is obtained. The results are therefore similar to those obtained with sodium stearate.

Fig. 6 shows density–temperature relations for technical sodium stearate of varying acidities. It is noted that there is no appreciable change due to the presence of the alkali. With the fatty acid, however, there appears to be a lowering of the complete melting point.

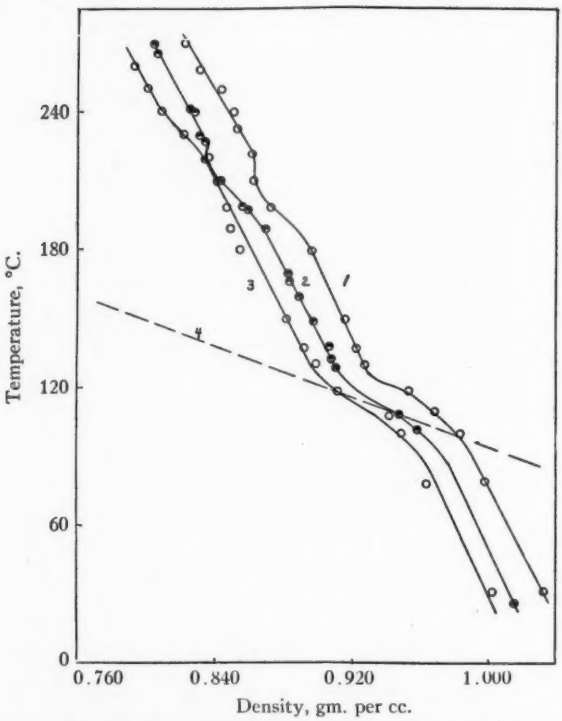

FIG. 6. *Effect of acidity and alkalinity on the density–temperature relation of sodium stearate. 2, Technical neutral sodium stearate alone; 3, with 10% free fatty acid; 1, with 2.5% of free alkali. Curve 4 shows for comparison the data of Lawrence obtained for sodium stearate.*

Discussion

An alteration in the physical state of sodium soaps might be expected as a result of the following agencies; (i) heat, (ii) polar solvents, (iii) non-polar solvents. The effect of heat was discussed in a previous communication, where indications of unidimensional and bidimensional melting points, a plasticity point, and complete melting point were obtained. The effect of moderate heat must be on the non-polar hydrocarbon chains only, the sodium carboxylic group remaining unaffected.

A non-polar mineral oil, such as an oil possessing a viscosity index of 95, is a solvent for the hydrocarbon portion of the soap only. The orienting effect of the polar grouping of the soap is such that this potential solvent

power has no appreciable effect. The density–temperature curve remains unaffected and is essentially the same as that of the soap alone, the non-polar oil acting only as an inert diluent. No lowering of the complete melting point is obtained.

Glycerol is a solvent for the sodium carboxylic grouping but exerts no effect on the non-polar hydrocarbon chain of the soap. Glycerol has no effect on the soap at ordinary temperatures, therefore, because of the orienting effect of the non-polar hydrocarbon chain on the polar grouping of the soap. It has been shown, for example (2), that the addition of large quantities of water to sodium stearate does not affect the lattice constants of the soap crystal or sharpness of the interferences obtained by X-ray analysis. Once the unidimensional melting point has been reached through the use of moderate heat, however, with the accompanying loosening of the lattice in one dimension, the orienting effect of the non-polar portion of the soap on the polar bonds is materially weakened, and the solvent power of glycerol on the polar bonds can be exerted. This solvent power will of course be greatly increased after the bidimensional melting point of the soap is attained. After the plasticity point has been passed, with the virtually complete loosening of non-polar bonds in the lattice, it is apparent that glycerol can act directly as a solvent. Melting of the soap crystal lattice and solubility in glycerol are closely related in this sense. The point of complete solution will of course depend on the amount of glycerol present. The magnitude of the effect of the glycerol at temperatures between the unidimensional melting point and the plasticity point of the soap (70° to 130° C.) will also depend on the amount of glycerol present. For example, 20% of glycerol is insufficient to bring about a change in the lower transition points as measured by differential cooling curves.

Polar types of mineral oil, e.g., oils of about 40 V.I. or less, act similarly to glycerol. It is shown in this work that large quantities of polar oil cause a gradual dissolution of the soap at relatively very low temperatures, all indications of phase transitions having disappeared.

It is possible that sodium soaps made plastic (i) by heat only and (ii) by a polar solvent with very moderate heat may differ in the character of the slip planes necessary for plasticity. In the case of (i), these slip planes must be between the ends of non-polar chains, whereas in the case of (ii), the polar bonds are disrupted and slip may occur parallel to the axis of the molecules rather than parallel to the basis plane of the crystal lattice.

Experimental

Differential cooling curve measurements were carried out according to methods previously described (1). The glycerol used was dehydrated to 99% purity by passing dry air through glycerol of sp. gr. 1.23 for about a week, the temperature being maintained at about 40° C.

The method previously described (1) for the determination of density of the soap alone was amended as follows for the two phase systems. The oil was introduced above the mercury by means of pressure through a fine capillary. The weight of oil added was obtained by measurement of the weight of mercury displaced, and the volume calculated from known specific gravity data, previously determined. The soap–oil mixture was heated to the temperature of apparent solution in order to effect a thorough dispersion of the mixture prior to the density determinations.

For the preparation of soaps of varying alkalinity and acidity, the soap was first analysed and the calculated quantity of acid or alkali added in alcoholic solution. The solution was then dried on a drum drier, and the soap film ground in a hammer mill.

The following shows inspection data for the two mineral oils used in this work*.

——	900 vis. 95 V.I. oil	900 vis. 40 V.I. oil
Gravity, A.P.I.	28.5	22.6
Flash, ° F.	510	455
Vis. at 100° F., S.U.S.	889.8	929.1
Vis. at 210° F., S.U.S.	81.0	68.3
V.I.	97	34
Neutralization No.	0.04	0.28
Robinson colour	9½	9½
Pour, ° F.	0	−10

Acknowledgment

This work was carried out under an arrangement between the Imperial Oil Limited and the National Research Council.

The authors wish to express their thanks to Imperial Oil Limited for permission to publish this paper.

References

1. GALLAY, W. and PUDDINGTON, I. E. Can. J. Research, B, 21 : 202-210. 1943.
2. THIESSEN, P. A., STAUFF, J., and WITTSTADT, W. Angew. Chem. 49 : 640-642. 1936.

* *Inspection data obtained from Imperial Oil Limited.*

THE RUBBER HYDROCARBON OF *ASCLEPIAS SYRIACA* L.[1]

By E. B. Paul[2], A. L. Blakers[2], and R. W. Watson[3]

Abstract

Milkweed latex collected in mid-July was coagulated in acetone, the coagulum purified, and the rubber examined by chemical and X-ray diffraction methods. Chromic acid oxidation analyses indicate that the monomer is isoprene. The X-ray evidence verifies these results and, further, fixes the polymer as the *cis*-configuration (rubber) as opposed to the *trans*-configuration (gutta-percha) of polyisoprene.

The solvent-extracted rubber from the leaves appears from the chromic acid oxidation results to be isoprene, but so far no polyisoprene diffraction diagram has been obtained. It is therefore likely that the solvent-extracted leaf rubber is an isoprene polymer of low molecular weight.

Introduction

The recent interest in rubber-bearing plants has led to the investigation of *Asclepias syriaca* (common milkweed). Since this plant yields a latex from which the rubber hydrocarbon can be obtained in a relatively pure state, a study of the nature and properties of this hydrocarbon was undertaken by physical and chemical means.

Milkweed latex was studied in 1849 by List (2). Marek (3) in 1903 subjected the latex to a detailed examination and reported its specific gravity to be 1.0278 to 1.0352 at 15°C., and its dry matter to be 17% by weight, made up mainly of inorganic salts, rubber (1.5%), and a mixture of esters of butyric and acetic acids, along with higher alcohols. Orlova (5) in 1932 reported similar values. Matsurevich (4) in 1935 made an extended investigation of the composition of the resins of milkweed latex. The specific gravity of the latex was reported to be 0.9900 at 27° C.

Collection of Latex

About 340 ml. of latex was collected in mid-July from wild stands in the Ottawa district. This was accomplished by removing the terminal shoot of the plant and collecting the few drops of latex in a bottle. The stem was then cut off about 2 in. below the initial cut, and this process repeated three to four times on each plant. In order to obtain sufficient latex, collections over a three day period were pooled.

The latex was protected from the sun as far as possible while in the field, and on arrival at the laboratory it was stored in the dark at about 5° C. However, a small quantity that was left at room temperature in a dark bottle

[1] *Manuscript received September 25, 1943.*

Contribution from the Divisions of Physics and Applied Biology, National Research Laboratories, Ottawa. Part of a joint investigation on the Rubber Content of Canadian Grown Plants being undertaken by the Department of Botany, University of Toronto, the Dominion Department of Agriculture, the Bureau of Mines, and the National Research Council of Canada. Issued as N.R.C. No. 1165.

[2] *Physicist, Division of Physics.*

[3] *Biochemist, Division of Applied Biology.*

without other special precautions had not seriously deteriorated in two months. Nevertheless during storage, coagulation, and at each subsequent step, care was taken to protect the rubber against oxidation and the action of light, e.g., during extraction nitrogen was bubbled continuously through the solution in the boiling flask, and the illumination intensity on the material was kept below 20 ft-c.

Methods

The pH was measured with a glass electrode, using a Coleman pH meter.

To obtain the dry weight, 5 ml. was dried *in vacuo* over calcium chloride at 25° C. for 24 hr., and transferred to a vacuum oven at 106° C. until the weight became approximately constant. The dried latex had the appearance of translucent waxy films mottled with brown. Methods for determining the percentage rubber hydrocarbon and resins in the latex are given below.

Properties of Latex

Some properties of milkweed latex determined from 3 to 10 days after collection are given in Table I. Changes due to bacterial action and other agencies may have occurred to some extent but at the low storage temperature are believed to be negligible.

TABLE I

PROPERTIES OF MILKWEED LATEX

Specific gravity at 25° C.	1.04
pH (average of two samples)	4.6
% Solids	23.5
% Rubber hydrocarbon (by wt.)	3.3
% Acetone soluble matter (resins)	14.3

Preparation of Rubber From Latex

Latex preserved at approximately 5° C. for several days after collection was poured slowly into four times its volume of a solution of 0.5% phenyl-betanapthylamine in reagent acetone through which nitrogen was kept bubbling. Precipitation was immediate, the coagulum forming a heavy, yellowish-brown ball. Little solid matter was left in suspension. The wet coagulum was transferred to a crystallizing dish, covered with a fresh solution of 0.5% phenylbetanapthylamine in acetone, and cut into small pieces. Extraction with warm acetone for 24 hr. was carried out in a Soxhlet fitted with a cellulose thimble lined with filter paper. The thimble and contents were dried *in vacuo* at 25° C. for 24 hr. Part of this acetone-extracted sample was used to obtain the pattern of Fig. 1. The percentage of impurities in this specimen (No. 4) may be judged from Table II.

PLATE I

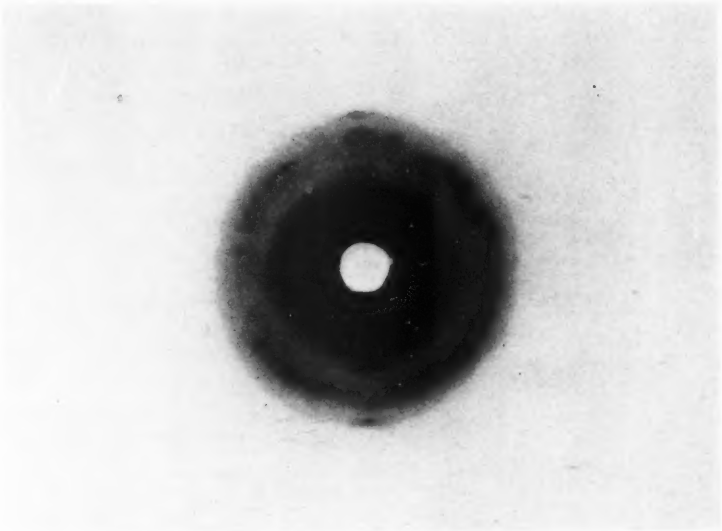

FIG. 1

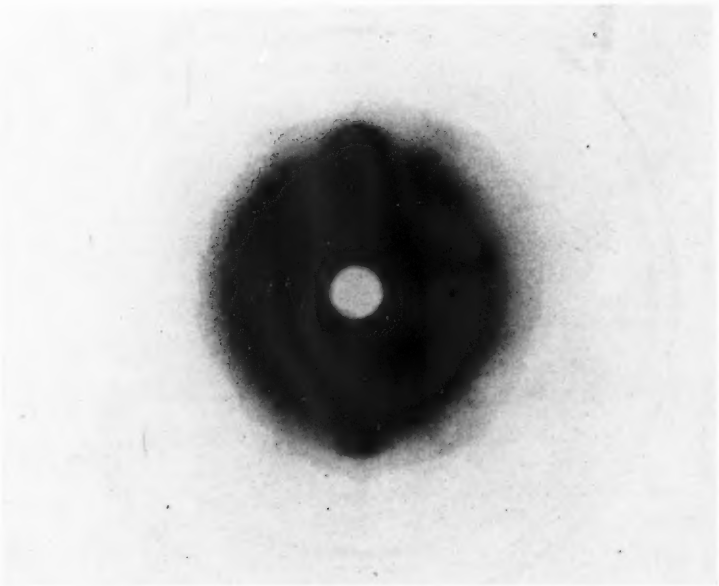

FIG. 2

TABLE II

RUBBER HYDROCARBON IN *Asclepias* RUBBERS

No.	Description of sample	Weight of sample, gm.	Titration, ml. (corrected)	Rubber hydrocarbon, %
1	Pale crepe	0.3321	34.73*	95.0**
2	Pale crepe	0.3487	36.57	95.2**
3	Milkweed latex rubber ppt'd. from benzene	0.3463	33.31	87.3
4	Acetone-extracted coagulum from milkweed latex	0.3170	19.12	54.8
5	Same as No. 4: boiled 1 hour in 2% NaOH, washed to pH 7.0, and dried	0.3407	32.42	86.4
6	Milkweed leaf rubber, solvent extracted, ppt'd. from benzene with acetone	0.3167	29.50	84.6
7	Milkweed leaf rubber, solvent extracted, ppt'd. from benzene with acetone	0.3267	29.90	83.1

* *Correction blanks applied throughout ranged from 0.30 to 0.34 ml.*
** *Accepted rubber hydrocarbon, 94 to 95%.*

A portion of this sample after benzene extraction for 24 hr. in a similar nitrogen-filled Soxhlet yielded about 0.2 gm. of cream-coloured rubber by precipitation with acetone.

Extraction of the same sample was continued for a further period of 48 hr. and the final solution concentrated in a vacuum still to about 15 ml. A viscous cream-coloured solution was obtained, suggesting the presence of a highly polymerized hydrocarbon. By precipitation with acetone 0.4 gm. of dry rubber was obtained. Digestion of 0.3463 gm. of this rubber (No. 3, Table II) in chromium-trioxide–sulphuric-acid and subsequent steam distillation and titration of the liberated acetic acid (1) showed 87% of rubber hydrocarbon as compared with 95% for pale crepe obtained with the same apparatus as a check on the method (Table II).

Purification of Acetone-Extracted Coagulum

From 115.72 gm. of latex a yield of 11.32 gm. of dried coagulum was obtained, and 2.30 gm. or 20.3% was found to be acetone soluble. The remaining 9.02 gm. was boiled with 2% sodium hydroxide for one hour, washed in several changes of boiling distilled water to a pH of 7.0, and dried *in vacuo* over calcium chloride at 25°C. for 24 hr.; it yielded 4.47 gm. of rubber. This sample was the one used for compounding. A similar sample (No. 5) gave 86% of rubber hydrocarbon by the chromic acid oxidation method (Table II).

Determination of the Resin Content of Latex

An analysis in which the resins dissolved at the time of coagulation in acetone were recovered, weighed, and added to the extract from the coagulum was made on a sample of 240 ml. of latex collected on August 12, 1943. The total acetone extract of this latex collection was found to be 14.3%. The pH after 22 days in storage was 4.6 and the specific gravity 1.037 at 25° C.

Compounding

About 4.5 gm. of rubber was available for compounding. This was carried out in the Rubber Laboratory of the Division of Chemistry, National Research Council. The following formula was used:

Milkweed rubber from latex	100.0 parts
Sulphur	2.5 parts
Zinc oxide	10.0 parts
Stearic acid	2.0 parts
D.P.G. (Diphenylguanidine)	1.5 parts

The batch was cured in a Schopper ring mould for 60 min. at 290° F. (143° C.). The X-ray diagram of Fig. 2 was obtained from pieces of the overflow.

The physical test data were based on the single Schopper ring and therefore can offer only an indication of the properties. They suggested that the milkweed rubber had higher modulus, lower set, lower tensile strength, and about the same elongation at break as a smoked sheet stock of the same formula.

Diffraction Studies

All diffraction patterns were recorded on flat film at 5 cm. from the specimen, using unfiltered cobalt radiation. Fig. 1 shows the pattern obtained with the acetone-extracted coagulum, stretched while wet to about 350% elongation. This shows the characteristic diagram of oriented polyisoprene. Most impurities seem to have been largely acetone soluble as their patterns do not appear. The sample precipitated from benzene solution also gave a weak polyisoprene diagram with elongated spots; this suggests that the rubber orients poorly after solution in benzene. The vulcanizate at an elongation of 450% gave the pattern of Fig. 2. This indicates well oriented polyisoprene and is identical with the diagram obtainable from the best smoked sheet stock.

Leaf Rubber

Two small samples of rubber (Nos. 6 and 7, Table II) were obtained from ground milkweed leaves by acetone–benzene extraction for a 24 hr. period with each solvent, followed by precipitation of rubber from benzene solution with methyl alcohol. They showed 85 and 83% of rubber hydrocarbon, respectively, after chromic acid oxidation. X-ray results failed to show the polyisoprene diagram.

Discussion

The density and percentage solids found in the present investigation (Table I) are both higher than those reported for European plants; the rubber content is more than twice that found by Marek (3) and Orlova (5), and the resin content was also found to be higher.

Marek (3) by analytical methods has found that the basic formula of the rubberlike constituent of this latex is C_5H_8. Orlova (5) also reached the same conclusion, basing her statement on the nature of the halogen derivatives of this substance. The chromic acid oxidation tests mentioned above confirm that the monomer is isoprene. The X-ray evidence verifies these results and further fixes the polymer as the *cis*-configuration (rubber) as opposed to the *trans*-configuration (gutta percha) of polyisoprene.

The solvent-extracted rubber from the leaves was examined by X-ray diffraction, but so far no polyisoprene diagram has been obtained. This does not prove that leaf rubber is not polyisoprene, but rather that attempts to orient it for the purposes of X-ray diffraction have been unsuccessful. The chromic acid oxidation results for leaf rubber indicate that the basic monomer is isoprene. Hence, it is likely that the solvent-extracted leaf rubber is an isoprene polymer of low molecular weight.

Acknowledgments

The writers' thanks are due to the staff of the Radiology Section of the Division of Physics for undertaking the tedious work of collection, to Mr. T. R. Griffith and Mr. J. R. Sheppard of the Rubber Laboratory of the Division of Chemistry for compounding the very small sample of rubber and for making the physical tests, and to Dr. N. H. Grace of the Applied Biology Division for advice and encouragement.

References

1. BURGER, V. L., DONALDSON, W. E., and BATY, J. A. Am. Soc. Testing Materials, Bull. 120 : 23-26. 1943.
2. LIST, C. Ann. 69 : 125-128. 1849.
3. MAREK, J. J. prakt. Chem. 68 : 385-416, 449-463. 1903.
4. MATSUREVICH, I. K. Zhur. Priklad. Khim. (J. Applied Chem. U.S.S.R.) 8(3) : 476-487. 1935.
5. ORLOVA, M. P. Trans. Mendeleev Congr. Theor. Applied Chem., 6th Congr. 2 : 753-760. 1932.

CANADIAN JOURNAL OF RESEARCH

Notes on the Preparation of Copy

General:—Manuscripts should be typewritten, double spaced, and the *original* and *one copy* submitted. Style, arrangement, spelling, and abbreviations should conform to the usage of this Journal. Names of all simple compounds, rather than their formulae, should be used in the text. Greek letters or unusual signs should be written plainly or explained by marginal notes. Superscripts and subscripts must be legible and carefully placed. Manuscripts should be carefully checked before being submitted, to reduce the need for changes after the type has been set. All pages should be numbered.

Abstract:—An abstract of not more than about 200 words, indicating the scope of the work and the principal findings, is required.

Illustrations

(i) *Line Drawings:*—Drawings should be carefully made with India ink on white drawing paper, blue tracing linen, or co-ordinate paper ruled in *blue* only. Paper ruled in green, yellow, or red should not be used. The principal co-ordinate lines should be ruled in India ink and all lines should be of sufficient thickness to reproduce well. Lettering and numerals should be of such size that they will not be less than one millimetre in height when reproduced in a cut three inches wide. If means for neat lettering are not available, lettering should be indicated in pencil only. All experimental points should be carefully drawn with instruments. Illustrations need not be more than two or three times the size of the desired reproduction, but the ratio of height to width should conform with that of the type page. The *original drawings* and one set of small but clear *photographic copies* are to be submitted.

(ii) *Photographs:*—Prints should be made on glossy paper, with strong contrasts; they should be trimmed to remove all extraneous material so that essential features only are shown. Photographs should be submitted *in duplicate;* if they are to be reproduced in groups, one set should be so arranged and mounted on cardboard with rubber cement; the duplicate set should be unmounted.

(iii) *General:*—The author's name, title of paper, and figure number should be written on the back of each illustration. Captions should not be written on the illustrations, but typed on a separate page of the manuscript. All figures (including each figure of the plates) should be numbered consecutively from 1 up (arabic numerals). Reference to each figure should be made in the text.

Tables:—Titles should be given for all tables, which should be numbered in Roman numerals. Column heads should be brief and textual matter in tables confined to a minimum. Reference to each table should be made in the text.

References should be listed alphabetically by authors' names, numbered in that order, and placed at the end of the paper. The form of literature citation should be that used in this Journal and titles of papers should not be given. All citations should be checked with the original articles. Each citation should be referred to in the text by means of the key number.

The *Canadian Journal of Research* conforms in general with the practice outlined in the *Canadian Government Editorial Style Manual*, published by the Department of Public Printing and Stationery, Ottawa.

DO NOT COPY